

Inter and Intra Molecular Phase Separation Environment Effects on PI-PEO Block Copolymers for Batteries & Fuel Cells

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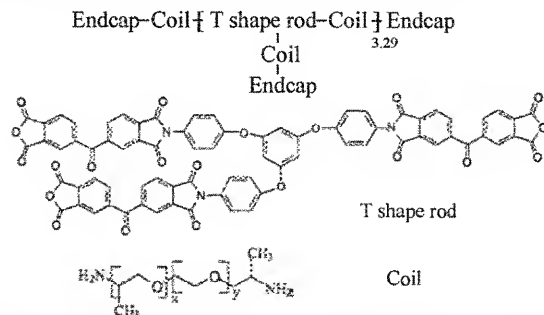
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Introduction

Rod-coil molecules have been introduced as a novel type of block copolymers with unique microstructure due to their ability to self-assemble to various ordered morphologies on a nanometer length scale¹. These molecules, comprised two homo polymers joined together at one end, microphase separate into ordered, periodic arrays of spheres, cylinders in the bulk state and or solution.^{2,3} To get ordered structure in a reasonable scale, additional force field are applied, such as mechanical shearing, electric field and magnetic field.^{1,4} Recently, progress has made it a possible to develop a new class of polyimides (PI)- Polyethylene oxide (PEO) that are soluble in polar organic solvents. The solvent-soluble PI-PEO has a wide variety of applications in microelectronics, since these PI-PEO films exhibit a high degree of thermal and chemical stability. In this paper, we report the self-assembled ordered structure of PI-PEO molecules formed from concentrate solution. The polymers consist of short, rigid rod T shape PI segments, alternating with flexible, PEO coil segments. The highly incompatible PI rods and PEO coils should phase separate, especially in the presence of lithium ions used as electrolytes for lithium polymer batteries. The rigid rod phase would provide a high degree of dimensional stability. Morphology of the phase separation has been observed by Small Angle x-ray (SAXS) and Atomic Force Microscopy (AFM).

Experimental

A series of PI-PEO molecules were synthesized and published elsewhere.⁵ One of the T-shape PI rods with alternating PEO coils was chosen for this study as-received. The chemical structure is shown in scheme 1. The sample was kept in vacuum before carrying out characterization and analysis. AFM (Digital Instrument Nanoscope IIIa) was used to examine the surface



Scheme 1. Structure of rod-coil polymer (The middle shows the T shape imide rod; The bottom shows the coil structure with Mw = 2000, x = 5 and y = 39.5).

topology of the self-assembled thin film. A 100 μm scanner was selected, and the contact mode was used to obtain both height and phase images. The force used by the cantilever was light enough to limit damage to the sample, yet heavy enough so that the surface features could be accurately explored. The scanning rate was controlled to be 1-3 Hz for low magnification images. The data were collected in 512×512 pixels per image. Two-dimensional (2D) SAXS experiments were performed at the synchrotron x-ray beam line X27C of the National Synchrotron Light Source in Brookhaven National Laboratory using imaging plates as detectors. The x-ray wavelength was $\lambda = 0.1307$ nm, and the scattering vector ($q = 4\pi \sin \theta / \lambda$, where 2θ is the scattering angle) were calibrated with silver behenate. 2D WAXD patterns were obtained from a Rigaku automated x-ray imaging system with 3000×3000 pixel resolution equipped with a cooling and heating hot stage. A Perkin-Elmer PYRIS Diamond DSC calibrated with indium and zinc standards analyzed the melting

crystallization behavior of PEO coil. Sample weight is 3.0 mg. isothermal melt crystallization kinetics were performed in situ as follows: the sample was quickly heated (at 100 $^{\circ}\text{C}/\text{min}$) up to 100 $^{\circ}\text{C}$, held there for 10 min to eliminate residue crystals, then the melt sample was cooled (at -180 $^{\circ}\text{C}/\text{min}$) to the designated crystallization temperature (T_c). The exothermal curve of heat of flow as function of time was recorded and investigated.

Results and Discussion

The solution self-assembled phase behavior of the PI-PEO has been examined with SAXS at room temperature, shown in Figure 1. A diffraction scattering halo with a d spacing of 13 nm is observed. It indicates that a microphase separation happened when the PI-PEO polymer was cast from solution in N-methylpyrrolidinone (NMP). As we know, the phase behavior of a bulk block copolymer really depends on three physical events, which compete with each other or override one over another in forming the final phase and crystalline morphologies in amorphous-crystalline block copolymers. They are the microphase separation of the block-copolymers at T_{ODT} , the crystallization of the crystallizable blocks at T_c^e , and the vitrification of the amorphous blocks at T_g^a . To form a microphase separated structure, T_{ODT} should be larger than T_g^a . While the TMA experiment results have shown that the T_g^a of PI is above 200 $^{\circ}\text{C}$ and the T_{ODT} is in the range of 80 $^{\circ}$ to 110 $^{\circ}$. It can safely be said that the microphase separation of this PI-PEO material is occurring in solution rather than in bulk state. Another direct evidence is provided by AFM phase (right) and height (left) images in Figure 2. In the phase image, some lamellar structures stack on the top on the other ones, as well as edge on behavior. The lamellar thickness measured from the height image is in the range from 11 to 15 nm, which is in agreement of the SAXS experiment result. AFM experiments were also performed below 10 $^{\circ}\text{C}$ (Figure 3). In the phase image, some PEO crystals are formed between (region A in Figure 3) and in (region B in Figure 3) the lamellas. In region A, the lamellas are edge on and expanded by PEO crystals with a dimension of 16 nm. In region B, actually in one lamella, the PEO crystallized in the lamella with dimension of 16 nm. To understand how the molecules self-assemble into this ordered structure, the molecular conformation of the crystallizable PEO coil and the amorphous PI rod must be studied first.

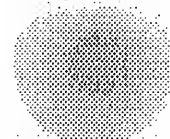


Figure 1. High-resolution synchrotron SAXS pattern.

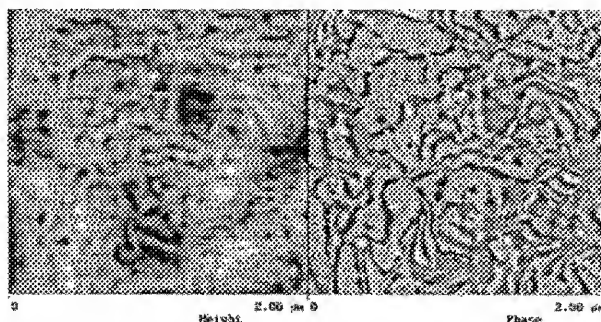


Figure 2. AFM Height (Left) and Phase image at room temperature.

In order to investigate the possible effects molecular architecture of PEO on this confined environment, a WAXD experiment has been carried out. Figure 4 demonstrates the typical WAXD pattern. The diffraction rings at $2\theta = 19^{\circ}$ come from the (120) plane, and the ring around $2\theta = 23^{\circ}$ is actually multiple diffraction rings with contributions from diffraction of several crystal planes. The linear PEO can be fitted into a monoclinic crystal structure. The unit cell parameters are $a = 0.805$ nm, $b = 1.304$ nm, $c = 1.948$ nm and $\beta = 125.4^{\circ}$.⁶ The repeating unit in a single chain shows a succession of trans, trans, gauche (*ttg*) conformations. The *ttg* conformation exhibits a $(7/2)$ helix with D_7 symmetry. D_7 indicates a dihedral molecular symmetry and subscript denotes a seven-fold screw axis parallel to the molecular axis. Since the period of the c-axis includes seven repeating units, each repeating unit

possesses a length of 0.278 nm in the crystalline portion. The average chain length, L is give by the following equation: $L = 0.278 \times M_n / 44$, where the 44 is the molecular weight of one PEO repeat unit. In our case, the extend PEO chain length is about 12.6 nm with molecular weight 2000.

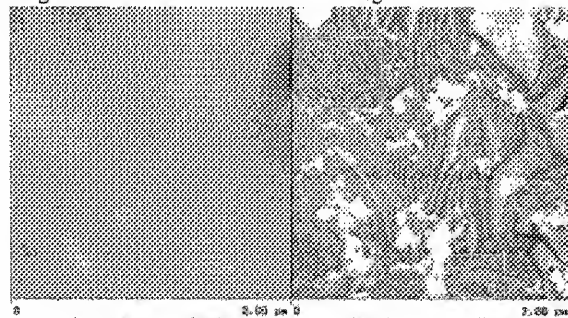


Figure 3. AFM Height (Left) and Phase (Right) image below 10 °C.

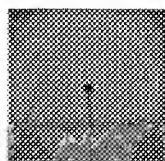


Figure 4. 2D WAXD pattern (The first reflection ring is (120) reflection. The second ring includes the (-130) , (032) , (-212) , (112) , (-124) and (004) reflections)

The computer simulation provides the T shape rod length parameter shown in Figure 5. The length of the rod in the main chain is 3.7 nm and the length of the rod in the side chain is 1.8 nm. By combining the molecular conformation and the AFM experiment results, a most possible microphase separation model has been provided (Figure 6). In this model, The T blocks represent the T shape rigid imide rods and the lines represent the extend PEO chains, respectively. Figure 6a is the side view of the lamellas, which are constructed by the main chain polymers. The side chains with rod and PEO crystals will separate the lamellas. This model depends on the inter molecular phase separation between PEO in side chains and imide rods in the main chain. The top view of the lamellas is shown in Figure 6b. The intra molecular phase separation between PEO crystals and imide rods will direct the main chains to form this kind of lamella.

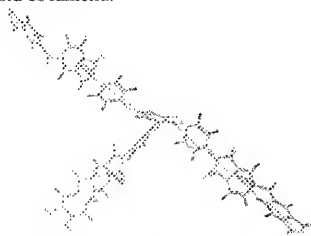


Figure 5. Computer simulation of T shape imide rod conformation

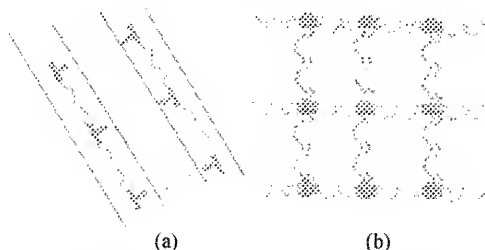


Figure 6. Most possible model (a) lamellar side view; (b) lamellar top view.

Is the PEO crystal growing in a lamella? Isothermal melt crystallization was studied by cooling the melt rapidly to a designated crystallization temperature (T_c). Heat flow curves were recorded as a function of time in

Figure 7. As the T_c increase, the crystallization exotherms shift to higher temperatures and became broad. The Avrami equation,⁷ which assumes that the relative degree of crystallinity (X_t) develops with time t , was used to analyze the isothermal crystallization process of PEO. The well-know double logarithmic plots $\log[-\ln(1-X_t)]$ vs. $\log(t)$ are shown in the Figure 8. Each curve shows an initial linear portion, subsequently tending to level off. This deviation was considered to be due to the secondary impingement in the later stage.⁸ The Avrami parameters n for PEO crystals determined from the initial linear portion in Figure 8 represents the PEO crystallization mechanism. The n values at different crystallization temperature are from 2.85 to 2.88, which indicate that the PEO is crystallized in a lamellar behavior.

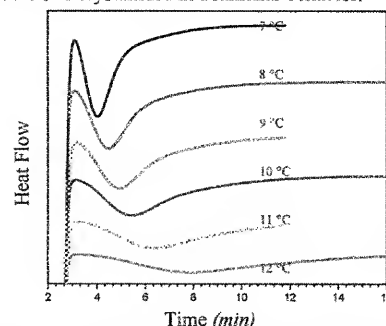


Figure 7. DSC curves of heat flow vs. time during isothermal crystallization (The numbers for the lines represent the crystallization temperatures)

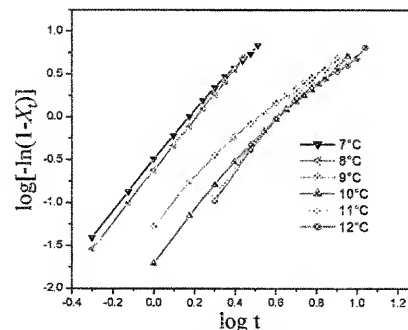


Figure 8. Plots of $\log[-\ln(1-X_t)]$ vs. $\log(t)$ for isothermal crystallization. (The numbers for the lines represent the crystallization temperatures)

Conclusions

In summary, the structural analysis via SAXS and AFM combined with the molecular conformation determined by WAXD and DSC experiments has provided experimental evidence to determine inter and intra molecular phase separation from the well-designed rod-coil block copolymer. A nano-confined environment is just simple vapor from a solution. It is clear that this environment will control PEO melting, crystallization behavior and make its possible applications, such as by blending with lithium oxide to form nano polymer electrolytes.

Acknowledgements. The authors would like to thank The University of Akron and the NASA Glenn Research Center for support of this project.

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